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An innovative approach for the simultaneous quantitative screening of organic plastic additives in complex matrices in marine coastal areas

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Abstract

Aiming the simultaneous determination of widely used organic plastic additives in complex marine matrices, this work proposes a fast and "green" analytical protocol based on quick, easy, cheap, effective, rugged, and safe (QuEChERS) technology. The validation of this innovative method on real matrices (i.e., sediments, mussel, fish, and *Posidonia oceanica*) indicated a general good performance in all of them for phthalate esters (PAEs), with low blank levels and average method recoveries varying from 54 ± 11 to $71\pm12\%$. The best method performance for organophosphate ester (OPE) flame retardants and plasticizers was in biotic matrices (recoveries 52 ± 31 to $86\pm38\%$). This application represents an innovative QuEChERS sequence of two dispersive solid-phase extraction (SPE) steps enabling this approach for the determination of important families of organic plastic additives in the marine environment. Indeed, our method allowed the fast screening and simultaneous determination of OPE and PAEs in various sites and matrices subject to different anthropogenic pressure in coastal NW Mediterranean Sea for the first time. Σ_7 PAE and Σ_9 OPE concentrations of 19-83 and 27-116 ng g⁻¹ dw (fish), of 80-714 and 42-71 ng g⁻¹ dw (mussels), of 192-908 and 47-151 ng g⁻¹ dw (*Posidonia oceanica*), and of 11-328 and 4-10 ng g⁻¹ dw (sediment) were measured, respectively. Our approach was sensible enough as to detect differences in the (bio)accumulation patterns of the target compounds in various species and/or sites. This application opens new perspectives for environmentally friendly marine environment monitoring and screening campaigns for organic plastic additives.

Keywords Organophosphate esters · Phthalates · QuEChERS · Marine vegetation · Biota · Sediments

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Introduction

Marine ecosystems, in particular coastal areas, are intricate yet delicate environments very sensitive to chemical contamination and generally under strong urban, agricultural, and industrial pressures (permanent or seasonal). One of the highest current concerns is on the environmental occurrence and potential effects of organic contaminants that could be released from plastic materials, due to the large accumulation of plastic waste in the marine environment (Jambeck et al. 2015). Organophosphate and phthalate esters (OPEs and PAEs, respectively) are among the most important organic plastic additives (Meeker et al. 2009; Hahladakis et al. 2018). Some OPEs and PAEs have been reported as hazardous chemicals and also classified (or suspected) endocrine disruptors (e.g., diethylhexyl phthalate, DEHP; tris-(2-chloro, 1-methylethyl) phosphate, TCPP) (van der Veen and de Boer 2012; Manikkam et al. 2013; Wei et al. 2015; Quinnies et al.

2017). Although these contaminants of emerging concern are commonly detected in the aquatic environment, their occurrence in marine ecosystems is less studied (Wei et al. 2015; Net et al. 2015a; Hermabessiere et al. 2017). In addition, data in complex marine matrices like sediments and particularly living organisms is scarce. This is mostly due to the challenges of the analytical determinations, with frequent problems such as high matrix effects and contamination of samples, with extraction and clean-up as critical steps (Namieśnik 2002; Baduel et al. 2015; Ibáñez and Cifuentes 2017). Single or different combinations of extraction/clean-up techniques have been employed for the analysis of OPEs and PAEs in some solid marine matrices (mostly sediments) like Soxhlet, accelerated solvent extraction (ASE), microwave and ultrasonic extraction (MAE and USE, respectively), with alumina, silica, and Florisil among the most common clean-up phases (David et al. 2006; Net et al. 2015b; Pantelaki and Voutsa 2019). The data for marine organisms is scarce (Hu et al. 2016; Greaves and Letcher 2017), typically involves intricate sample cleanup procedures and the existing analytical protocols generally consider OPEs and PAEs separately. Aiming for the simplification of this type of analysis and the reduction of their environmental fingerprint (Gałuszka et al. 2013), we present here a fast and "green" method based on QuEChERS (quick, easy, cheap, effective, rugged, and safe) (Anastassiades et al. 2003) for the simultaneous assessment of OPEs and PAEs in various complex marine matrices. Namely, sediment, mussel, fish, and the seagrass Posidonia oceanica are all collected in the Mediterranean Sea, one of the major hotspots of plastic contamination in the world (Eriksen et al. 2014; Cózar et al. 2015). This strategy is innovative and represents an improvement to the current trends and state-of-the-art of the QuEChERS technology (Santana-Mayor et al. 2019) and to the multi-component quantification of emerging contaminants in marine ecosystems.

Experimental

Solvents, standards, and QuEChERS materials

Information on solvents, standards, and materials is available in Supporting Information (Text S1), together with additional details on compounds, GC/MS identification, and physical-chemical properties (Table S1).

Samples

Four different marine matrices collected in 2018 in the NW Mediterranean Sea were chosen in this study: *Posidonia oceanica* (leaves), an autochthonous seagrass, mussels, fish, and sediments. *Posidonia oceanica* and sediments were selected from two different locations with distinct anthropogenic

signatures (Figure S1). The first sampling area is in the southern part of Marseille bay, not far from the touristic sea route between the city and the Frioul archipelago (sample named Frioul). The other area is under the influence of the Marseille's WWTP discharge (named WWTP-Cortiou). Mussels (Mytilus galloprovincialis) were taken in the wild (Figure S1) and also purchased in a supermarket (commercial). Fish adult individuals were chosen from two different species, Atlantic bonito (Sarda sarda, Bloch, 1793) and European hake (Merluccius merluccius, Linneaus, 1758) and were acquired in Marseille's fish market (dorsal muscle dissected for analyses). Both species are commercialized for human consumption and can be found both in the Atlantic and in the Mediterranean. All the samples were then frozen at -20 °C and freeze-dried. Biotic samples were ground into a homogenized fine powder and sediments sieved (500 µm) prior to analyses (see Text S1 for further details).

General QuEChERS protocol

Several experiments were conducted in this study, first to adapt a previously developed approach based on commercial QuEChERS to the target emerging contaminants and marine matrices and then to validate the final protocol. Typically, the QuEChERS base technique is composed of three main phases (Homem et al., 2013; Ribeiro et al. 2014): (i) a microscale extraction (in this case, sonication) of the matrix in a closed tube using an organic solvent; (ii) addition of anhydrous salts or buffers to the tube with the matrix and extract to promote the separation of phases and facilitate the partitioning of the analytes into the organic phase (first QuEChERS stage, Q1); (iii) transfer of the Q1 extract to a new tube containing appropriate sorbents to perform a dispersive-SPE used as a clean-up step to remove undesired components (second QuEChERS stage, Q2). The general QuEChERS protocol used in the current study is an adaptation of this approach.

A scheme is detailed in Fig. 1, and the final selection of clean-up phases is discussed on the "QuEChERS composition evaluation" section (Fig. 2). Briefly, all samples were spiked with surrogate-labelled standards (100 ng sample⁻¹) (Table S1) and placed (0.5 g dw and 3 g dw for biota and sediment, respectively) in centrifuge tubes. The corresponding solvent mix was then added (10 mL), as well as a small amount of activated copper for sediments only. The tubes were closed with Teflon liner caps, vortexed (1 min), and then ultrasound extracted (10 min). Then, the contents of Q1 were added to the extraction tubes and the mixture vortexed (3 min) and centrifuged (5 min at 4000 rpm). The supernatant was transferred with pre-cleaned Pasteur pipettes to another tube containing the sorbents selected for Q2 and processed as above. Finally, the extract was concentrated to about 50 µL using a gentle N2 stream and the syringe standards for quantification were added (100 ng sample⁻¹) (Table S1).

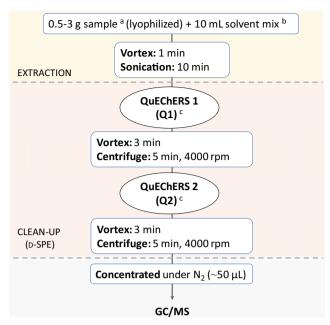


Fig. 1 General QuEChERS protocol used for the quantitative analysis of OPEs and PAEs. (a) Different sample amounts were used depending on the matrix, (b) different solvent combinations and (c) compositions of Q1 and Q2 were tested (see "QuEChERS composition evaluation" section)

Instrumental analysis

Samples were analyzed by gas chromatography coupled with mass spectrometry (GC/MS) for nine organophosphate esters and seven phthalate esters (Table S1), in selected ion monitoring (SIM) and electron impact (EI, 70 eV) modes. The separation was achieved in a 30 m \times 0.25 mm i.d. \times 0.25 μm HP-5MS capillary column (Agilent J&W). All target contaminants were quantified by the internal standard (IS) procedure based on multi-level calibration curves. The injection volume was of 2 μL with the helium flow at 1 mL min $^{-1}$. The temperatures of the MS transfer line, ion source, and quadrupole were 300, 230, and 150 °C, respectively. Further details are presented in Text S1.

Quality assurance/quality control

Given the strong possibility of cross-contamination during OPE and PAE analysis, strict measures were taken to

minimize it. The entire protocol was carried out in an ISO class 6 cleanroom for organic trace analysis. The use of plastic material was avoided at all times and all glassware was carefully cleaned, and baked at 450 °C for 6 h. Florisil, alumina, and MgSO₄ were also baked at 450 °C overnight before use. Method blanks considering all steps were made for each batch of analysis. Median blank levels in the real samples analyzed were generally low, varying from non-detected (n.d.) to ~ 8 ng depending on the compound and the extraction batch, with the exception of TCPP-2 which exhibited higher blank levels (69 ng) (Table S2). Results were blank corrected accordingly by subtracting the blank value of the specific batch. Chromatographic peaks were considered only with signal-tonoise ratio \geq 10. The instrumental LOQs obtained were at pg level, varying from 1 to 30 pg for OPEs and from 1 to 10 pg for PAEs (see Table S3 for further details).

Results and discussion

Upgrading of commercial QuEChERS

Extraction solvent and material

Preliminary experiments were conducted to adapt a protocol based on the commercial QuEChERS developed previously for the analysis of methylsiloxanes in marine vegetation (Rocha et al. 2019) to the extraction of OPEs and PAEs from the target matrices. The focus was on the effects of the extraction tube material and solvent mixtures on the background noise and blank levels, which are critical issues for the trace analysis of organic plastic additives. Polypropylene Falcon tubes (PP, 50 mL) and glass centrifuge tubes (30 mL) were tested under five solvent conditions (in duplicate) with no samples or sorbents: (a) Hexane/DCM (1:1); (b) DCM; (c) DCM/acetone (2:1); (d) EtOAc; (e) DCM/EtOAc (1:1). The chromatograms were evaluated by tracking the presence of all target compounds, focusing on those normally showing blank problems (i.e., DEHP for PAEs and TCCP for OPEs) (Guo and Kannan 2012; Stubbings et al. 2017) (Table S4). Both DEHP and TCPP were found in all PP extracts, whereas TCPP was not found in the extracts from glass tubes. The

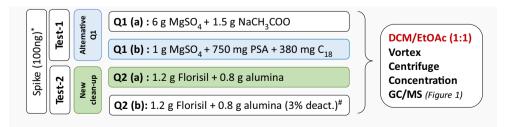


Fig. 2 Scheme illustrating the different QuEChERS combinations studied for the optimization of the general procedure for the analysis of OPE and PAEs in complex marine matrices. Asterisk indicates native and

surrogate compounds were spiked at 100 ng tube⁻¹. Number sign indicates the alumina was deactivated using MQ water

DEHP values were from 2 to 36 times higher in the extracts from PP compared with those of glass material (except in one assay with DCM/acetone (2:1) with similar values). In addition, chromatograms from the PP extracts of all solvent conditions showed considerably higher background noise (Figure S2). These facts confirm that the classic Falcon PP tubes used in QuEChERS protocols should not be used in the analyses of PAE and OPEs, nor probably for other organic plastic additives. In glass tubes, EtOAc and DCM/EtOAc (1:1) exhibited the lowest DEHP blank levels. However, since TDCP was found in one of the EtOAc replicates, the choice of the best solvent relied on DCM/EtOAc (1:1).

QuEChERS composition evaluation

A first test was performed to replicate the QuEChERS composition reported previously for marine vegetation (Rocha et al. 2019), but in this case using glass tubes (instead of polypropylene), lyophilized samples (instead of wet samples), and DCM/EtOAc (1:1) as extraction solvent. However, this approach failed to produce clean extracts. To improve the method, two different combinations, each of commonly used clean-up sorbents on the analysis of target compounds in environmental samples (van der Veen and de Boer 2012; Castro-Jiménez et al. 2018), were tested (in duplicate and with no sample) for Q1 and Q2 steps (Fig. 2). In each case, the sorbent combinations were inserted in glass tubes and spiked directly (100 ng) with target compounds (natives and surrogates) and extracted with DCM/EtOAc (1:1) following the general procedure described in the "General QuEChERS protocol" section (Fig. 1). Test-1 (for Q1): The original protocol developed for fresh matrices (Rocha et al. 2019) included a combination of sodium acetate (NaCH₃COO) and anhydrous MgSO₄ in Q1 stage (Q1-a). However, our new application considers freeze-dried samples in order to facilitate homogenization, sample handling, and comparability, and NaCH₃COO could be not needed. This test evaluated the effect of the substitution of a traditional Q1 stage by a combination of anhydrous MgSO₄, primary and secondary amine (PSA) and C₁₈, which is typically used in commercial QuEChERS but on a second stage, resulting in an alternative Q1 (Q1-b) for this application. This modification makes way for a second cleanup step, not included in commercial QuEChERS, which would then become the second stage (Q2) for our application (Fig. 2). Test-2 (for Q2): In this step, the resulting extract from Q1 is added to a tube containing two possible combinations of Florisil and alumina (Q2-a with activated alumina and Q2-b with deactivated alumina) to evaluate a potential enhancement of the clean-up capacity of the entire protocol (Fig. 2).

Median recoveries ranged from 77 to 91% for PAEs and 52 to 67% for OPEs depending on the condition (Figure S3). Overall, for Q1, the results indicate that Q1-b (i.e., 1 g $MgSO_4 + 0.75 \text{ g PSA} + 0.38 \text{ g } C_{18}$) yield similar or better results than the common first step of QuEChERS approaches (Q1-a): 6 g MgSO₄ + 1.5 g NaCH₃COO, particularly for OPEs. Regarding Q2 (1.2 g Florisil +0.8 g alumina), similar recoveries were obtained using activated (Q2-a) and 3% deactivated alumina (Q2-b) for most compounds (Figure S3). Since the deactivation process is timeconsuming and may increase the variability of the results, it was decided to pursue with activated alumina. These results pointed towards the adoption of conditions Q1-b and Q2-a, which now represent an innovative QuEChERS sequence of two dispersive-SPE steps instead of the common salt/buffer (Q1) and dispersive-SPE (Q2) combination.

Validation in marine matrices

The application of the optimized QuEChERS protocol to real samples included validation via recovery and repeatability assays on *Posidonia*, mussels, fish (*Sarda sarda*), and sediments. Triplicate recovery tests were done at two spiking levels (25 and 100 ng sample⁻¹) with 0.5 g of dry sample, except for sediments where 3 g was used (Table 1). Results indicated acceptable average recoveries at both spiking levels in all samples both for PAEs (54 ± 11 to $71 \pm 12\%$, average \pm SD) and for OPEs in biotic samples (52 ± 31 to $86 \pm 38\%$). Lower recoveries were obtained for OPEs in sediment samples, varying from 40 ± 9 to $41 \pm 6\%$. Average (n = 3) relative standard deviations ranged from 3 to 10%, indicating a good method repeatability (Table S5).

The use of simpler and faster techniques in the trace analysis of organic pollutants of emerging concern in complicated environmental matrices often requires a careful consideration regarding the potential reduction of performance (in terms of recovery, for instance) as opposed to the saving of resources and time and the reduction of harmful substances employed in the process (organic solvents, etc.). Our results and the wide scope of the protocol clearly justify its adoption. However, we acknowledge the possibility of future improvement of its validation parameters, particularly on its application on sediment for the OPE analysis.

Screening of OPEs and PAEs in field samples

The newly developed protocol was used to perform an initial screening of the presence of OPEs and PAEs in naturally contaminated samples from the four matrices in the study. $\Sigma_7 \text{PAE}$ concentrations in sediment (11–328 ng.g⁻¹ dw) were 3–33 times higher than $\Sigma_9 \text{OPE}$ levels (4–10 ng.g⁻¹ dw) (Table S6). Higher PAE and OPE levels were generally found in the sample collected

Table 1 Recoveries (average ± SD) for OPE and PAE extraction from four marine matrices at two spiking levels (25 and 100 ng sample⁻¹)

AV R (%) $(n = 3)$ Spike level	Sediment		Posidonia		Mussel		Fish	
	25 ng	100 ng	25 ng	100 ng	25 ng	100 ng	25 ng	100 ng
Organophosphate e	sters (OPEs)							
TPP	28.9 ± 2.9	31.4 ± 1.0	45.3 ± 2.5	32.7 ± 0.7	57.5 ± 4.7	34.2 ± 2.8	37.3 ± 2.6	32.1 ± 0.7
TiBP	34.4 ± 3.0	40.3 ± 1.2	43.9 ± 2.8	42.3 ± 2.7	84.3 ± 6.1	49.1 ± 4.4	79.1 ± 1.4	53.1 ± 1.6
TnBP	35.2 ± 2.3	38.7 ± 1.5	68.1 ± 2.0	47.2 ± 0.1	74.5 ± 8.4	45.4 ± 2.0	69.6 ± 1.2	48.1 ± 1.3
TCEP	57.0 ± 16.9	32.0 ± 0.8	26.3 ± 4.5	24.3 ± 2.3	44.4 ± 3.0	28.5 ± 2.9	26.4 ± 4.8	22.9 ± 1.5
TCPP*	43.1 ± 4.3	43.8 ± 2.8	18.0 ± 4.9	45.2 ± 7.8	101.8 ± 145	34.5 ± 2.8	37.1 ± 6.3	32.6 ± 1.3
TDCP	48.5 ± 1.5	45.5 ± 2.3	135.5 ± 0.3	60.1 ± 1.5	139.9 ± 3.1	58.7 ± 6.5	29.8 ± 1.3	37.7 ± 2.1
TPhP	45.1 ± 3.0	43.8 ± 0.8	41.6 ± 2.9	42.4 ± 2.2	44.1 ± 2.9	40.6 ± 2.1	49.3 ± 2.7	45.0 ± 1.7
EHDPP	37.8 ± 3.3	50.1 ± 2.2	72.2 ± 4.5	71.1 ± 2.2	78.3 ± 4.8	67.7 ± 5.3	73.8 ± 2.4	70.2 ± 3.8
TEHP	31.5 ± 0.7	44.4 ± 2.9	151.4 ± 10.4	137.2 ± 0.5	148.0 ± 20.2	125.6 ± 12.8	133.4 ± 3.1	126.5 ± 0.4
Average OPEs	40.2 ± 9.0	41.1 ± 6.2	66.9 ± 46.8	55.8 ± 33.4	85.9 ± 37.9	53.8 ± 29.7	59.5 ± 33.9	52.0 ± 31.2
D27-TBP	35.1 ± 2.3	36.2 ± 0.6	56.2 ± 1.8	56.2 ± 1.1	57.7 ± 1.8	52.9 ± 9.1	57.3 ± 1.2	57.0 ± 1.4
D15-TDCP	37.6 ± 1.8	38.0 ± 0.4	70.7 ± 1.0	68.9 ± 2.0	78.0 ± 1.3	65.5 ± 14.3	71.8 ± 1.5	71.1 ± 2.2
Phthalic acid esters (PAEs)								
DMP	37.3 ± 3.6	47.5 ± 5.1	66.7 ± 2.2	46.1 ± 2.6	73.8 ± 1.3	48.9 ± 2.8	73.5 ± 1.2	57.9 ± 2.7
DEP	51.5 ± 18.4	46.5 ± 0.8	61.1 ± 3.9	46.0 ± 3.0	52.2 ± 1.7	46.3 ± 1.7	48.8 ± 1.2	51.4 ± 2.8
DiBP	53.7 ± 7.2	59.3 ± 1.5	44.8 ± 7.4	42.7 ± 1.1	62.4 ± 0.6	51.3 ± 0.7	55.0 ± 0.7	54.0 ± 2.1
DnBP	54.6 ± 2.8	67.5 ± 1.1	$\mathbf{n.r} \pm \mathbf{n.r}$	$\text{n.r} \pm \text{n.r}$	75.8 ± 19.9	52.1 ± 6.5	57.6 ± 5.1	53.2 ± 3.5
BBzP	54.9 ± 11.3	48.0 ± 3.0	86.8 ± 2.4	64.5 ± 2.0	91.6 ± 1.8	53.5 ± 1.8	90.7 ± 1.7	60.0 ± 2.4
DEHP	75.4 ± 31.2	61.0 ± 4.3	$56.5 \pm n.r$	59.3 ± 40.1	72.0 ± 0.0	63.7 ± 8.4	55.3 ± 4.5	50.5 ± 2.0
DnOP	49.2 ± 3.9	55.7 ± 0.5	82.3 ± 2.4	77.9 ± 1.5	70.3 ± 0.8	69.8 ± 1.6	76.7 ± 1.9	76.3 ± 4.3
Average PAEs	53.8 ± 11.3	55.1 ± 8.1	66.4 ± 15.9	56.1 ± 13.7	71.2 ± 12.1	55.1 ± 8.5	65.4 ± 15.2	57.6 ± 8.9
D4-DnBP	49.3 ± 2.3	51.8 ± 0.4	65.5 ± 0.7	66.5 ± 1.9	68.8 ± 1.8	62.6 ± 5.0	64.1 ± 1.9	64.6 ± 2.4

^{*}TCPP values correspond to the most abundant isomer, TCPP-1; n.r., not reported due to analytical problems

in the WWTP vicinity (Cortiou) compared with Frioul (Fig. 3(a, b)), particularly for DEHP (76 times higher). PAE and OPE total concentrations were dominated by DEHP and TCPP in Cortiou, respectively, while DiBP and EHDPP were more abundant in Frioul. On the contrary, \sum_7 PAE concentrations (908 ng g⁻¹ dw) in *Posidonia oceanica* were 19-fold higher than \sum_9 OPE levels (47 ng g⁻¹ dw) in Frioul, while similar total concentrations were obtained near the WWTP for PAEs and OPEs (192 and 151 ng g⁻¹ dw, respectively), pointing to different environmental sources and accumulation rates. DEHP dominated in both sites, while TCPP was one of the most abundant OPEs but prevailed only in Frioul (Fig. 3(c, d)).

In fish samples, Σ_7 PAE and Σ_9 OPE concentrations were similar, varying from 19 to 83 ng g⁻¹ dw, and from 27 and 116 ng g⁻¹ dw, respectively (Table S6). However, the bioaccumulation patterns were different, with individual OPEs (dominated by TDCP) at higher concentrations in the Atlantic bonito, while PAEs were generally more abundant in the European hake, with DnBP predominating (Fig. 3(e, f)). These results suggest different biomagnification potential

of the two families of organic plastic additives studied. $\Sigma_7 PAE$ concentrations in mussel (80–714 ng g⁻¹ dw) were 2–10 times higher than $\Sigma_9 OPE$ (42–70 ng g⁻¹ dw) (Table S6), indicating a generally higher potential of bioaccumulation for phthalates in this organism. Wild mussel exhibited similar or higher levels than commercial mussels for all PAEs, particularly DEHP (12-fold higher) (Fig. 3(g, h)). This trend was not so clear for OPEs, with higher values in commercial mussel for some OPEs like TCEP and EHDPP. The mandatory depuration process for mussel commercialization for health safety guidelines (Lee et al. 2008) could result in a general contaminant reduction in the organism and partially explain these results, particularly for PAEs. OPEs have been reported as persistent (Wei et al. 2015) and may not be affected at the same rate for the depuration process.

Conclusions

Our study points to QuEChERS as a valid approach for the simultaneous quantitative screening of OPE and PAE in

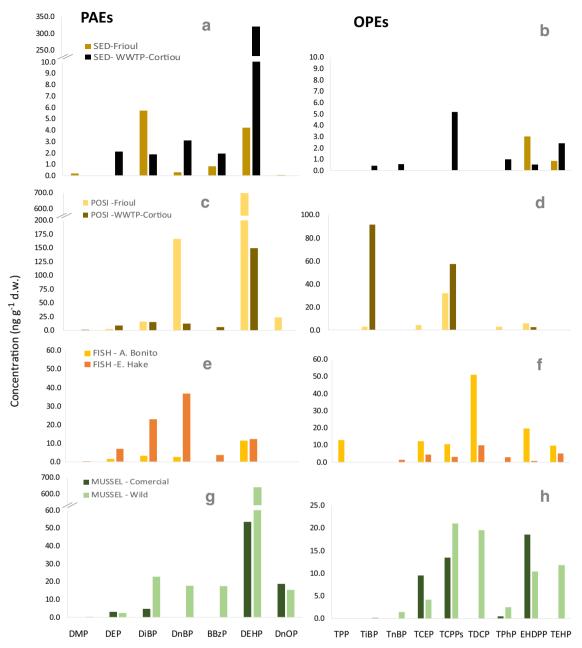


Fig. 3 OPE and PAE concentrations in sediment, Posidonia oceanica, fish, and mussel samples from NW Mediterranean Sea

complex marine matrices. However, a number of modifications in commercial QuEChERS are required for this application, like the use of glass tubes instead of classical polypropylene Falcon tubes and the introduction of additional cleanup phases like Florisil and alumina in the protocol. This application represents an innovative QuEChERS sequence of two dispersive-SPE steps enabling this approach for the determination of important families of organic plastic in the marine environment. Indeed, even if a limited number of samples were analyzed in this work, the developed method allowed the simultaneous determination of OPE and PAEs in various matrices and sites under different anthropogenic pressure in

coastal NW Mediterranean Sea (fish, mussel, and *Posidonia* levels assessed for the first time). Our innovative approach was sensible enough as to detect differences in the (bio)accumulation patterns of the target compounds in various species and/or sites, launching new perspectives for more sustainable monitoring and screening strategies to address organic plastic additives in the marine environment.

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